

# Vapor–Liquid Equilibria for Methanol + Poly(ethylene glycol) 250 Dimethyl Ether

J. Herraiz, Shubao Shen,<sup>†</sup> and A. Coronas\*

Department of Mechanical Engineering, Universitat Rovira i Virgili, Cra de Salou s/n, 43006 Tarragona, Spain

Vapor–liquid equilibria  $P$ ,  $T$ ,  $x$  for the methanol + poly(ethylene glycol) 250 dimethyl ether (PEGDME 250) binary system were obtained by the static method in the range of temperatures from 293.15 K to 423.15 K at 10 K intervals. A modified Barker's method was used to accurately calculate the liquid and vapor composition from the overall composition of the sample, the measured pressure and temperature, and the Redlich–Kister expression for the excess Gibbs free energy of the liquid phase at each temperature. The obtained  $P$ ,  $T$ ,  $x$  data were correlated by the NRTL and UNIQUAC temperature-dependent activity coefficient models using the maximum likelihood method. This system shows nearly ideal behavior at lower temperatures but negative deviation at higher temperatures. Also with the increase in temperature and composition of poly(ethylene glycol) 250 dimethyl ether, the logarithm of activity coefficients of methanol becomes more negative. The excess molar enthalpy was calculated using the Gibbs–Helmholtz equation and the NRTL and UNIQUAC parameters at 303.15 K and compared with experimental data existing in the literature.

## Introduction

Organic mixtures such as tetraethylene glycol dimethyl ether (2,5,8,11,14-pentaoxapentadecane, TEGDME or E181) with 2,2,2-trifluoroethanol (Bockelmann and Renz, 1983; Seher and Stephan, 1983; Stephan and Hengerer, 1993) and poly(ethylene glycol) 250 dimethyl ether (PEGDME 250), TEGDME, or glycerol with methanol (Stüven, 1989; Boer et al., 1994; Boer, 1995) have been suggested as working pairs in absorption heat pumps or heat transformers. These kinds of mixtures are noncorrosive, completely miscible in a wide temperature range, and thermally stable up to 200 °C, with low working pressures. Methanol + PEGDME 250 might be a promising working pair for high-temperature heat pump applications. Also, poly(ethylene glycol) dimethyl ethers have been proved successful for scrubbing waste air and gas streams containing different organic substances because of their low vapor pressure, low viscosity, and good dissolving power for many organic substances, acid gases, and even inorganic compounds.

This paper is a continuation of our study on new binary systems to be used in absorption cycles for upgrading waste heat to useful higher temperature levels. Here we reported vapor–liquid equilibria (VLE) data for the system methanol + PEGDME 250 from 293.15 K to 423.15 K at 10 K intervals and pressures up to 1 MPa. In a previous work (Esteve et al., 1995), VLE data for methanol + TEGDME covering the same pressure and temperature ranges were published.

## Experimental Section

**Materials.** Poly(ethylene glycol) 250 dimethyl ether (Aldrich, 99+%) is a mixture of poly(ethylene glycol) dimethyl ethers  $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ , where  $n = 3$  to 9. The product used in the present study was analyzed by

gas chromatography and mass spectrometry, with the following percent compositions: for  $n = 3$ , 14.19%;  $n = 4$ , 16.97%;  $n = 5$ , 22.76%;  $n = 6$ , 21.93%;  $n = 7$ , 12.99%;  $n = 8$ , 8.51%, and  $n = 9$ , 2.64%. The molecular weight of this product is 283.33. Methanol (Fluka, >99.8%) and PEGDME 250 were used with no further purification, but they were thoroughly degassed by several freezing and thawing cycles and stored over type 4A molecular sieves.

**Apparatus.** The total vapor pressures of the binary mixtures were measured by a static method (Pemberton and Mash, 1978; Chaudhari et al., 1995). The apparatus was described in Esteve et al. (1995). It consists of an equilibrium cell, a double-walled thermostat bath with a 25 L capacity filled with silicon oil (BASYLON M20 from Bayer), a differential pressure null transducer (DPT) (Ruska model 2439-702), a precise pressure controller (Ruska model 3891-801), and a Haake proportional temperature controller for the bath. The measuring systems are a digital pressure gauge (Ruska model 6242), a Pt100 platinum resistance thermometer (Anton Paar, MKT 100), and a Mettler electronic balance with an accuracy of  $\pm 0.1$  mg for weighing the pure components. The overall reproducibility of the pressure measurement was better than  $\pm 0.1$  kPa. The temperature in the bath was controlled better than  $\pm 0.01$  K up to 373.15 K and  $\pm 0.02$  K above 373.15 K, and the accuracy of liquid mole fraction is better than  $\pm 0.0001$ .

**Procedure.** The experimental procedure, which included the load of the sample, the measurement of the vapor pressure, and the calculation accurately of the cell volume, was also described by Esteve et al. (1995).

## Data Reduction

To obtain accurate vapor–liquid equilibrium  $P$ ,  $T$ ,  $x$  data from the initially input composition of the samples and the measured vapor pressure and temperature at an equilibrium state, Barker's method (Barker, 1953) was modified to reduce the experimental data. In this approach, an

\* Author to whom all the correspondence should be addressed. E-mail: ACORONAS@ETSEQ.URV.ES.

<sup>†</sup> Visiting Professor leaving from Nanjing University of Chemical Technology, Nanjing 210009, China.

**Table 1. Saturated Molar Volume  $V_m$ , Vapor Pressure  $P^s$ , and Second Virial Coefficients Used in the Present Study for Ethanol (1) + Water (2) at 313.15 K**

	ethanol	water
$V_m/10^6/\text{m}^3 \text{ mol}^{-1}$	59.58	18.14
$P^s/\text{kPa}$	17.908	7.359
$B_{ij}/10^6/\text{m}^3 \text{ mol}^{-1}$	-2096	-1160
$B_{ij}/10^6/\text{m}^3 \text{ mol}^{-1}$	-1140	

**Table 2. Experimental  $P$ ,  $x_1$ , and Estimated  $y_1$  for Ethanol (1) + Water (2) at 313.15 K**

$P/\text{kPa}$	$x_1$	$y_1$	$\Delta P = P^{\text{calc}} - P$	$\Delta y = y_1^{\text{calc}} - y_1$
12.34	0.0953	0.4489	0.086	0.0037
14.56	0.1901	0.5555	0.283	0.0053
15.43	0.2795	0.6013	0.162	0.0035
16.00	0.3699	0.6321	0.078	-0.0026
16.57	0.4711	0.6631	0.073	-0.0044
16.92	0.5608	0.6943	-0.024	-0.0075
17.33	0.6599	0.7378	-0.038	-0.0085
17.68	0.8037	0.8261	-0.145	-0.0037
17.86	0.9141	0.9176	-0.102	0.0023

expression for the excess Gibbs free energy ( $G^E$ ) of the liquid phase was assumed and parameters in this expression were obtained by fitting  $P$ ,  $x$  data at each temperature. An orthogonal  $n$  degree polynomial Redlich-Kister form was used for the  $G^E$  model in this work

$$G^E/(x_1 x_2 RT) = A_1 + A_2(x_1 - x_2) + A_3(x_1 - x_2)^2 + \dots + A_n(x_1 - x_2)^{n-1}$$

A Marquardt's nonlinear regression program was applied to estimate the  $A_k$  parameters, minimizing the following objective function

$$\text{OF} = \sum_i^N \left| \frac{(P^{\text{calc}} - P)}{P} \right|_i^2$$

where  $P$  is the experimental pressure and  $N$  is the number of experimental points for a temperature.

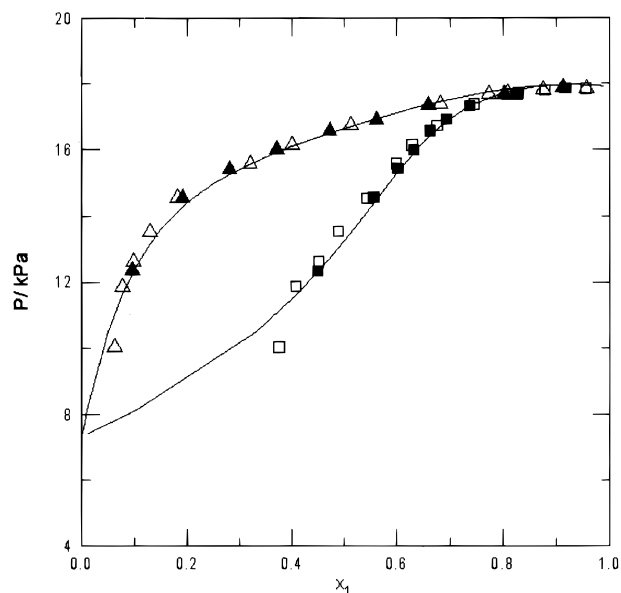
The corrections from overall input cell composition to actual liquid-phase composition at equilibrium were made at each temperature. Also in this procedure, the vapor-phase nonideal behavior was taken into account by using the virial equation of state truncated at the second virial coefficient, estimated from the correlation of Tsonopoulos (1974). Therefore, vapor-phase compositions in the cell were also estimated.

The performance of the apparatus and the described data reduction procedure were tested by measuring the vapor-liquid equilibria for ethanol + water at 313.15 K. The values of the molar volumes, second virial coefficients, and vapor pressures of the pure components used in the calculations are listed in Table 1. Our experimental isothermal  $P$ ,  $x$  data with the estimated vapor-phase composition results are reported in Table 2 and shown in Figure 1.

In Figure 1 and Table 3, our results can be compared with the experimental  $P$ ,  $T$ ,  $x$ ,  $y$  data measured by Mertl (1972). The selected data had been passed through both area and point thermodynamic consistency tests (Gmehling and Onken, 1991). From both the table and the figure, it can be seen that our experimental results were in very good agreement with literature data.

## Results and Correlation

The vapor pressure correlations from Reid et al. (1988) for methanol and from Conesa et al. (1996) for PEGDME

**Figure 1.** Experimental vapor pressures of ethanol (1) + water (2) at 313.15 K and correlated by the NRTL equation from the Dortmund Data Bank (Gmehling and Onken, 1991): □,  $y_1$  Mertl (1972); ■,  $y_1$  this work; △,  $x_1$  Mertl (1972); ▲,  $x_1$  this work; —, NRTL DDB.**Table 3. Absolute Average Deviations of the Pressure AADP and the Vapor Composition AADY of the Present Study and Mertl (1972) Calculated by the NRTL Equation<sup>a</sup>**

	this work	Mertl (1972)
AADP <sup>b</sup> /kPa	0.1102	0.2268
AADY <sup>c</sup>	0.0043	0.0055

<sup>a</sup> The NRTL parameters were taken from the Dortmund Data Bank (Gmehling and Onken, 1991). <sup>b</sup> AADP =  $(1/N) \sum_i^N |P_{\text{exp}} - P_{\text{NRTL}}|_i$ . <sup>c</sup> AADY =  $(1/N) \sum_i^N |y_{\text{exp}} - y_{\text{NRTL}}|_i$ .

**Table 4. Molecular Weight, Critical Temperature, Pressure, and Molar Volume, Acentric Factor, and UNIQUAC Parameters,  $r$ ,  $q$ , and  $q'$ , of Methanol and PEGDME 250**

	methanol	PEGDME 250
$M_r$	32.04	283.33
$T_c/\text{K}$	512.58	749.07
$P_c/\text{MPa}$	8.094	2.651
$V_c/10^6/\text{m}^3 \text{ mol}^{-1}$	118.0	789.0
$\omega$	0.0537	0.982
$r$	1.43	10.60
$q$	1.43	9.04
$q'$	0.96	9.04

250 were used. The critical temperature, pressure, volume, and acentric factor for methanol had been taken from the Reid et al.'s (1988) property data bank; for PEGDME 250 these properties had been estimated using group contributions methods (Leonidas and Rafiqul, 1994) for each component from  $n = 3$  to  $n = 9$ , and then the true critical properties of the PEGDME 250 mixture were estimated by the method of Chueh and Prausnitz (1967). The liquid molar volumes for each compound were calculated from the density-temperature correlations (Smith and Srivastava, 1986; Conesa et al., 1996). Table 4 summarizes these properties for methanol and PEGDME 250.

The vapor pressures of the methanol + PEGDME 250 system were measured by Esteve (1995). The vapor liquid equilibrium data for methanol + PEGDME 250 are given in Table 5. The  $P$ ,  $T$ ,  $x$  data were correlated by tempera-

**Table 5. Experimental Vapor Pressure and Liquid Mole Fraction and Estimated Vapor Mole Fraction and Activity Coefficient of Methanol for the System Methanol (1) + PEGDME 250 (2) at Different Temperatures**

P/kPa	x <sub>1</sub>	y <sub>1</sub>	γ <sub>1</sub>	P/kPa	x <sub>1</sub>	y <sub>1</sub>	γ <sub>1</sub>	P/kPa	x <sub>1</sub>	y <sub>1</sub>	γ <sub>1</sub>	P/kPa	x <sub>1</sub>	y <sub>1</sub>	γ <sub>1</sub>
T = 293.15 K				T = 303.15 K				T = 313.15 K				T = 323.15 K			
1.21	0.0842	0.9809	1.0946	1.79	0.0841	0.9742	0.9609	2.76	0.0841	0.9685	0.9129	4.080	0.0841	0.9620	0.8591
2.25	0.1586	0.9904	1.0771	3.37	0.1586	0.9872	0.9627	5.23	0.1586	0.9844	0.9199	7.78	0.1586	0.9814	0.8760
3.26	0.2370	0.9940	1.0600	4.98	0.2370	0.9922	0.9644	7.76	0.2370	0.9905	0.9289	11.71	0.2371	0.9889	0.8962
4.29	0.3196	0.9959	1.0441	6.61	0.3196	0.9948	0.9666	10.51	0.3196	0.9938	0.9375	16.08	0.3196	0.9928	0.9151
5.35	0.3990	0.9971	1.0312	8.29	0.3990	0.9963	0.9694	13.30	0.3990	0.9956	0.9438	20.40	0.3990	0.9949	0.9289
6.35	0.4799	0.9978	1.0206	10.16	0.4799	0.9974	0.9730	16.00	0.4799	0.9968	0.9487	24.90	0.4799	0.9964	0.9389
7.30	0.5556	0.9984	1.0129	11.85	0.5556	0.9980	0.9770	18.65	0.5556	0.9977	0.9531	28.65	0.5556	0.9974	0.9458
8.42	0.6428	0.9988	1.0066	13.80	0.6428	0.9987	0.9824	21.91	0.6428	0.9984	0.9595	33.82	0.6428	0.9982	0.9535
9.33	0.7167	0.9992	1.0032	15.33	0.7167	0.9990	0.9873	24.46	0.7167	0.9989	0.9670	38.17	0.7167	0.9987	0.9618
10.50	0.8071	0.9995	1.0009	17.50	0.8071	0.9994	0.9931	27.58	0.8071	0.9993	0.9790	43.32	0.8071	0.9993	0.9752
11.51	0.8826	0.9998	1.0001	19.02	0.8826	0.9997	0.9971	30.99	0.8826	0.9997	0.9899	48.79	0.8826	0.9996	0.9879
12.30	0.9608	0.9999	1.0000	20.77	0.9608	0.9999	0.9996	33.55	0.9608	0.9999	0.9986	52.77	0.9608	0.9999	0.9982
12.50	0.9703	0.9999	1.0000	21.26	0.9703	0.9999	0.9998	34.57	0.9703	0.9999	0.9991	54.14	0.9703	0.9999	0.9990
T = 333.15 K				T = 343.15 K				T = 353.15 K				T = 363.15 K			
5.950	0.0841	0.9558	0.8226	8.510	0.0841	0.9495	0.7944	11.81	0.0841	0.9431	0.7636	16.12	0.0841	0.9366	0.7393
11.38	0.1586	0.9786	0.8498	16.28	0.1586	0.9752	0.8124	22.74	0.1587	0.9724	0.7967	31.03	0.1587	0.9692	0.7713
17.26	0.2371	0.9872	0.8703	24.26	0.2371	0.9851	0.8346	34.57	0.2371	0.9835	0.8218	47.25	0.2371	0.9816	0.7998
23.64	0.3196	0.9916	0.8863	33.75	0.3196	0.9904	0.8579	47.45	0.3196	0.9893	0.8422	65.10	0.3196	0.9881	0.8253
29.90	0.3990	0.9941	0.8991	43.11	0.3990	0.9933	0.8787	60.64	0.3990	0.9925	0.8597	83.42	0.3991	0.9917	0.8469
37.21	0.4799	0.9958	0.9120	53.89	0.4799	0.9953	0.8979	76.14	0.4799	0.9947	0.8781	104.85	0.4799	0.9942	0.8679
42.97	0.5556	0.9970	0.9250	62.71	0.5557	0.9966	0.9145	89.34	0.5557	0.9962	0.8972	123.26	0.5557	0.9958	0.8880
50.78	0.6428	0.9980	0.9418	74.10	0.6428	0.9977	0.9334	105.49	0.6428	0.9975	0.9215	146.98	0.6428	0.9972	0.9127
57.51	0.7167	0.9986	0.9572	84.45	0.7167	0.9985	0.9499	120.70	0.7167	0.9983	0.9434	168.25	0.7167	0.9981	0.9351
65.61	0.8071	0.9992	0.9762	96.83	0.8072	0.9991	0.9706	139.16	0.8072	0.9991	0.9692	195.19	0.8072	0.9990	0.9630
73.93	0.8826	0.9996	0.9898	109.82	0.8827	0.9996	0.9866	157.80	0.8826	0.9995	0.9871	222.17	0.8826	0.9995	0.9838
80.20	0.9608	0.9999	0.9987	118.84	0.9608	0.9999	0.9982	172.01	0.9608	0.9999	0.9984	243.60	0.9608	0.9999	0.9979
82.42	0.9703	0.9999	0.9992	121.51	0.9703	0.9999	0.9989	175.5	0.9703	0.9999	0.9991	246.59	0.9703	0.9999	0.9987
T = 373.15 K				T = 383.15 K				T = 393.15 K				T = 403.15 K			
21.64	0.0841	0.9304	0.7197	28.46	0.0841	0.9240	0.7002	36.70	0.0841	0.9174	0.6806	46.90	0.0841	0.9113	0.6674
41.47	0.1587	0.9660	0.7514	54.23	0.1587	0.9626	0.7300	69.87	0.1587	0.9592	0.7110	88.45	0.1587	0.9557	0.6945
63.21	0.2371	0.9796	0.7787	83.00	0.2371	0.9776	0.7593	106.95	0.2372	0.9755	0.7402	135.60	0.2372	0.9733	0.7224
87.40	0.3196	0.9868	0.8037	115.11	0.3197	0.9855	0.7876	149.12	0.3197	0.9841	0.7687	189.55	0.3197	0.9826	0.7510
112.61	0.3991	0.9908	0.8264	148.96	0.3991	0.9899	0.8131	193.10	0.3991	0.9890	0.7953	246.06	0.3991	0.9879	0.7787
141.17	0.4799	0.9936	0.8502	186.39	0.4799	0.9929	0.8383	241.40	0.4799	0.9927	0.8228	307.07	0.4800	0.9915	0.8079
167.20	0.5557	0.9954	0.8741	222.04	0.5557	0.9950	0.8626	289.66	0.5557	0.9945	0.8501	371.52	0.5557	0.9940	0.8372
200.29	0.6428	0.9970	0.9038	267.55	0.6428	0.9967	0.8924	350.85	0.6428	0.9964	0.8839	452.18	0.6428	0.9961	0.8736
231.07	0.7167	0.9980	0.9302	307.61	0.7167	0.9978	0.9197	408.64	0.7167	0.9976	0.9144	529.20	0.7167	0.9974	0.9066
268.50	0.8072	0.9989	0.9616	361.77	0.8072	0.9988	0.9538	477.72	0.8072	0.9987	0.9517	621.44	0.8072	0.9986	0.9472
305.54	0.8827	0.9995	0.9837	412.33	0.8827	0.9994	0.9795	546.34	0.8827	0.9994	0.9790	712.08	0.8827	0.9993	0.9769
337.30	0.9608	0.9998	0.9979	457.40	0.9608	0.9998	0.9973	609.59	0.9608	0.9998	0.9973	799.30	0.9608	0.9998	0.9970
340.69	0.9703	0.9999	0.9988	462.35	0.9703	0.9999	0.9984	617.00	0.9703	0.9999	0.9984	811.56	0.9703	0.9999	0.9982
T = 413.15 K				T = 423.15 K											
58.86	0.0841	0.9049	0.6530	73.00	0.0841	0.8985	0.6412								
110.32	0.1587	0.9523	0.6803	135.70	0.1587	0.9486	0.6664								
169.50	0.2372	0.9710	0.7063	208.70	0.2372	0.9686	0.6906								
237.39	0.3197	0.9810	0.7330	292.61	0.3197	0.9793	0.7163								
306.80	0.3991	0.9867	0.7601	377.15	0.3991	0.9855	0.7435								
382.60	0.4800	0.9907	0.7906	467.80	0.4800	0.9898	0.7752								
467.78	0.5557	0.9934	0.8228	581.00	0.5558	0.9928	0.8094								
573.95	0.6429	0.9957	0.8637	717.44	0.6429	0.9953	0.8535								
673.97	0.7167	0.9972	0.9006	846.21	0.7167	0.9969	0.8935								
795.58	0.8072	0.9985	0.9451	1004.6	0.8072	0.9984	0.9414								
914.30	0.8827	0.9993	0.9766												
914.30	0.9608	0.9998	0.9970												

ture-dependent five-parameter NRTL and four-parameter UNIQUAC equations, as follows

NRTL

$$\ln \gamma_i = x_j^2 \left( \tau_{ji} \left( \frac{G_{ji}}{x_i + x_j G_{ji}} \right)^2 + \frac{\tau_{ij} G_{ij}}{(x_j + x_i G_{ij}^2)} \right)$$

$$\tau_{ij} = C_{ij} / (RT)$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij})$$

$$C_{ij} = C_{ij}^C + C_{ij}^T (T - 273.15)$$

UNIQUAC

$$\ln \gamma_i = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + \phi_j \left( l_i - \frac{r_i}{r_j} l_j \right) - q_i \ln(\theta'_i + \theta'_j \tau_{ji}) + \theta'_j q_j \left( \frac{\tau_{ji}}{\theta'_i + \theta'_j \tau_{ji}} - \frac{\tau_{ij}}{\theta'_j + \theta'_i \tau_{ij}} \right)$$

$$\phi_i = \frac{x_i r_i}{x_i r_i + x_j r_j}; \quad \theta_i = \frac{x_i q_i}{x_i q_i + x_j q_j}; \quad \theta'_i = \frac{x_i q'_i}{x_i q'_i + x_j q'_j}$$

$$\tau_{ij} = \exp(-C_{ij} / (RT)); \quad C_{ij} = C_{ij}^C + C_{ij}^T (T - 273.15)$$

where  $i = 1, j = 2$  or  $i = 2, j = 1$

In both cases the vapor-phase behavior was calculated from the virial equation of state truncated at the second virial coefficient. The values of the volume parameter  $r$

**Table 6. Parameters of NRTL and UNIQUAC Equations for the Methanol + PEGDME 250 System**

	$C_{12}^C/\text{J mol}^{-1}$	$C_{12}^T/\text{J mol}^{-1} \text{K}^{-1}$	$C_{21}^C/\text{J mol}^{-1}$	$C_{21}^T/\text{J mol}^{-1} \text{K}^{-1}$	$\alpha_{12}$
NRTL	255.1	-4.18	-22.90	-8.23	3.55
UNIQUAC	-904.22	-3.59	4075.5	-0.75	

**Table 7. Root-Mean-Square Deviations (rmsd) and the Variance,  $s$ , of the Fit for Methanol + PEGDME 250 Using NRTL and UNIQUAC Equations**

	rmsd/kPa	rmsd/K	rmsd/ $x_1$	$s$
NRTL	0.19	0.04	0.0015	18.01
UNIQUAC	0.18	0.03	0.0014	16.58

and the surface area parameter  $q$  and  $q'$  needed in the UNIQUAC equation for methanol were taken from Prausnitz et al. (1980) and for PEGDME 250 from López (1996).

The parameters were fitted using the maximum likelihood principle (Prausnitz et al., 1980) in order to minimize the function

$$s = \sum_i \left[ \frac{(P^{\text{calc}} - P)^2}{\sigma_P} + \frac{(T^{\text{calc}} - T)^2}{\sigma_T} + \frac{(x^{\text{calc}} - x)^2}{\sigma_x} \right]_i$$

where  $P$  is the pressure,  $T$  the temperature, and  $x$  the liquid mole fraction of methanol. The standard deviations  $\sigma_P$ ,  $\sigma_T$ , and  $\sigma_x$  for  $P$ ,  $T$ , and  $x$  were taken as 0.1 kPa, 0.02 K, and 0.0005, respectively.

The fitting parameters and root-mean-square deviations in  $P$ ,  $T$ ,  $x$  are given in Tables 6 and 7, respectively. The agreement was excellent for both equations. The experimental vapor pressure data for all the isotherms are plotted in Figure 2 along with the data calculated using the UNIQUAC equation for comparison.

We attempted to calculate the excess molar enthalpy  $H^E$  from the vapor pressure data using the Gibbs–Helmholtz equation and the NRTL and UNIQUAC parameters. The calculated and experimental  $H^E$  values at 303.15 K (Esteve et al., 1994) are plotted in Figure 3 for comparison.

## Discussion

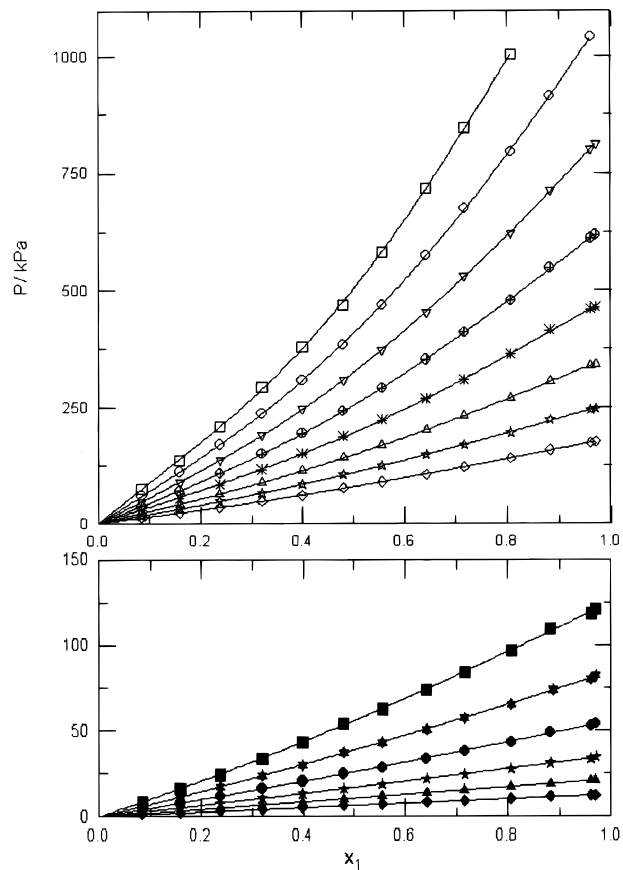
The VLE data indicated that this binary system showed nearly ideal behavior at 293.15 K whereas negative deviations at higher temperatures were observed. The logarithm of activity coefficients of methanol became more negative with the increase in temperature and mole fraction of PEGDME 250.

The excess molar enthalpy at 303.15 K was positive in the whole range of composition, having a maximum of about 625 J mol<sup>-1</sup> at  $x_1 = 0.6$ . At all mole fractions the predicted values from NRTL and UNIQUAC equation were always higher. The UNIQUAC equation predicted a maximum value of 1425 J mol<sup>-1</sup> at  $x_1 = 0.55$  and NRTL a maximum value of 1072 J mol<sup>-1</sup> at  $x_1 = 0.55$ .

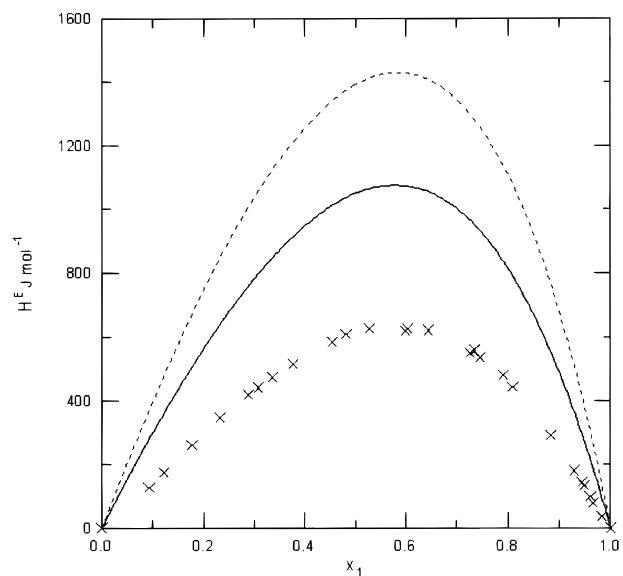
## Conclusion

A modified Barker method was successfully applied to accurately calculate the liquid and vapor composition at the equilibrium state from the total pressure and injected sample composition and temperature. The system ethanol + water was used to validate the methodology.

In this paper VLE data for methanol + PEGDME 250 from 293.15 K to 423.15 K over the entire composition range were obtained following the method developed. The NRTL and UNIQUAC temperature-dependent equations were used to fit them. The results obtained were satisfac-



**Figure 2.** Experimental and calculated vapor pressure data of the methanol + PEGDME 250 system as a function of the liquid mole fraction of methanol at different temperatures:  $\blacklozenge$ , 293.15 K;  $\blacktriangle$ , 303.15 K;  $\blackstar$ , 313.15 K;  $\bullet$ , 323.15 K;  $*$ , 333.15 K;  $\blacksquare$ , 343.15 K;  $\diamond$ , 353.15 K;  $\star$ , 363.15 K;  $\triangle$ , 373.15 K;  $*$ , 383.15 K;  $\oplus$ , 393.15 K;  $\nabla$ , 403.15 K;  $\circ$ , 413.15 K;  $\square$ , 423.15 K; —, calculated by UNIQUAC equation.



**Figure 3.** Experimental ( $\times$ ) and calculated from VLE using NRTL parameters (—) and UNIQUAC (---) excess molar enthalpy data for methanol + PEGDME 250 at 303.15 K as a function of the liquid mole fraction of methanol.

tory. The calculated excess enthalpies at 303.15 K from VLE overestimated the experimental values. The deviations for UNIQUAC were higher than for NRTL.

This binary system showed more negative deviations at higher temperatures, which may be good for the operation

of high-temperature absorption heat pumps using this working pair.

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